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TINTING GLAZE WITH IRON-CONTAINING COMPOUNDS ON NONFIRED INORGANIC MATERIALS

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The possibility of obtaining tinted glazes without the synthesis of iron-bearing pigments is considered. Fine particles of an iron-based alloy, for instance steel obtained by fine milling of metal working waste, are introduced in the glaze composition. The testing of a glaze suspension based on window glass cullet with additives of white-burning clays and finely milled carbon steel chips demonstrate that this suspension after firing yields a uniformly tinted coating.

Glazing of articles made of various inorganic materials is finding ever increasing applications. Apart from glazing of traditional ceramics, various technologies for glazing concrete products have been developed. Unlike ceramics, concrete items cannot be completely placed into a firing furnace due to the presence of hydrate water in cement stone. It is proposed to fire glaze on concrete using screen furnaces or the induction discharge flame of a gas burner [1, 2].

Glazing of ceramics and nonfired materials uses various colorant pigments, including those containing F_2O_3 as a chromophore. It is known that the maximum effect in the formation of a tint depends on the electromagnetic radiation absorption spectrum, which is a light flux due to the electron transfer between the chromophore ion and oxygen, i.e., the emergence of charge transfer bands [3]. The emergence of color bands is related to photon absorption due to a charge transfer with the transition of an electron from the oxygen ion to the central ion (usually a transition element, such as Fe, Mn, Cr, Co, Ti, etc.), the transition of an electron from ions of the same metal in different valence states in their complexes ($Fe^{3+} – O^{2–} – Fe^{2+}$, $Mn^{4+} – O^{2–} – Mn^{2+}$, $Ti^{4+} – O^{2–} – Ti^{3+}$, etc.), and the formation of redox complexes with ions of different variable-valence metals ($Fe^{3+} – O^{2–} – Mn^{2+}$, $Mn^{4+} – O^{2–} – Fe^{2+}$, $Ti^{4+} – O^{2–} – Fe^{2+}$, $Mn^{4+} – O^{2–} – Ti^{3+}$) [3]. The presence of these elements in a glaze contributes to a better chemical interaction between the glaze layer and the article surface (due to ion substitution) and the emergence of a transition layer.

It is advisable to use variable-valence metals (iron, cobalt, nickel, chromium, manganese, etc.) as colorant components in glazes for nonfired materials, since they have a high tinting capacity and a favorable effect on the physicochemical properties of glazes intended for deposition on nonfired materials. The most preferable compounds are oxides, but other compounds are possible as well, such as sulfides, sulfates, chlorides, nitrates, and also microparticles of some metals [4]. Tinted metal compounds can be introduced directly in a raw glaze batch or in frit melting.

At the same time, tinted glazes can be obtained as well without synthesizing relatively expensive iron-bearing pigments.

In this study it is proposed to introduce Fe_2O_3 for glaze tinting in the form of fine particles of iron-based alloys, for instance, steel particles produced by fine milling of metal working waste (chips, filings, etc.) [5]. Standard carbon-bearing steel contains (here and elsewhere, wt.%): 0.06 – 0.62 carbon, 0.25 – 0.90 manganese, not more than 0.35 silicon, not more than 0.05 phosphor, not more than 0.07 sulfur, and the rest iron [6]. In small quantities MnO increases the chemical resistance and decreases the viscosity and crystallization propensity of a vitreous melt. An increase in SiO_2 content raises the viscosity of silicate melts and the chemical resistance of the coating in any media, and expands the viscosity interval [7]. The total content of the components (carbon, phosphor, and sulfur), whose presence in the glaze in undesirable, is insignificant.

Glaze suspensions based on cullet of clear window sheet glass with 5% additive of white-burning clay and 0.35% finely milled (residue on No. 008 sieve not more than 0.5%) carbon steel chips were prepared by the standard technology. The fusing of the glaze deposited on ceramics was performed in an electric furnace at a temperature of 800°C with an exposure of 30 min. The glaze deposited on concrete was fixed by means of a gas burner treatment (temperature around 2000°C) for 5 min.

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After fusion the colors of uniformly tinted glaze coatings were estimated visually. The coating obtained in the electric furnace had a dark brown color, and the coating fused with a gas burner had a gray-green color. The different colors of coatings depend on the properties of iron compounds under different fusion conditions. Along with iron oxidation

$$3Fe + 2O_2 \rightarrow Fe_3O_4;$$

$$Fe_3O_4 \rightarrow FeO + Fe_2O_3,$$

in the course of heating of steel particles, iron carbide contained in steel reacts with air oxygen and the oxygen-containing glaze components:

$$Fe_3C + O_2 \rightarrow 3Fe + CO_2.$$

Since hematite (Fe_2O_3) that has a rhombic lattice consisting of six O^{2-} atoms and four Fe^{3+} atoms is steady only up to 1000°C [8] and the fusion of the article surface with a burner occurs at a significantly higher temperature, it can be assumed that iron for a while exists in the form of [FeO_4] and [FeO_6] in ferrous spinel, which, however, is an unstable compound:

$$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2;$$

$$Fe_3O_4 \rightarrow FeO + Fe_2O_3.$$

In this case the color changes from brown to black and then to gray-green.

Thus, the possibility of producing glaze coatings by using iron-based alloy particles directly as a colorant component without the synthesis of pigments has been substantiated.

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